

MELTING BEHAVIOR OF COAL ASH MATERIALS FROM COAL ASH COMPOSITION

by

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INTRODUCTION

The melting behavior of coal ash materials is characterized by several temperatures relating to stages of deformation of cone-shaped ash samples on heating. Viscosity of coal ash melts through the molten temperature range is also useful for characterization. This information has been used primarily for design of steam generation equipment, but may be usefully extended to coal conversion processes such as gasification. Coal ash does not melt sharply like a pure compound, but rather softens over a temperature range as the temperature is increased. As it melts, the heated ash exhibits a plastic range between the solid and mobile liquid states. The temperature range corresponding to the plastic state, as well as viscosity and melting phenomena, depend on the composition of the ash and the gaseous environment. Studies of the melting and viscosity of ash melts over a range of temperatures and gaseous environments have demonstrated this dependence.^{1,2,3}

The purpose of this paper is to provide some framework for understanding the observed behavior, and to suggest use of a concept that should be helpful in further studies of that behavior.

Acids and Bases

The melting and viscosity behavior has been described as a function of the composition of the coal ash in terms of acids and bases. The acids have been defined as oxides of Al, Si, and Ti, while the bases were oxides of Na, K, Ca, Mg, and Fe.

The structural inorganic chemical characteristics of the acids and bases will be of interest in establishing the reasons for labels such as acid or base, and in understanding the impact of the acid or base characteristics on the melting or viscosity properties of coal ash.

Inorganic cations may be characterized by ionic radii for their common valences. In general, the radii decrease with charge, and also with atomic weight for a given valence. The radii, according to Ahrens, for the inorganic cations indicated above are listed below in Angstrom units:

Si ⁺⁴	0.42	Fe ⁺²	0.74
Al ⁺³	0.51	Na ⁺¹	0.94
Fe ⁺³	0.64	Ca ⁺²	0.99
Mg ⁺²	0.67	K ⁺¹	1.33
Ti ⁺⁴	0.68		

The two values are given for iron because of the importance of both valence states.

In crystals, and in some cases for liquids, the cations are surrounded by a specific number of anions. This coordination number is determined by the ratio of the radii of the two oppositely charged species. A coordination number of four produces a tetrahedron and is expected between radius ratio limits of 0.225 and 0.414. A coordination number of six produces an octahedron and is expected between radius ratio limits of 0.414 and 0.732. The coordination number of eight is expected for somewhat larger radius ratios.

In coal ash the predominant anion is the oxide ion. Using a radius of 1.40 Å for the oxide and applying the radius ratio criteria, tetrahedral coordination is expected for cations with a radius smaller than 0.58 Å or specifically Si⁺⁴ and Al⁺³. The octahedral configuration is expected for cations between 0.58 and 1.03 Å or Fe⁺³, Mg⁺², Ti⁺⁴, Fe⁺², Na⁺¹, and Ca⁺². The remaining K⁺ would be expected to have a cubic configuration with coordination number eight. Under proper conditions, these coordination numbers would be expected in melts.

Ionic Potential

Another useful concept is the ionic potential which is defined as the quotient of the valence and ionic radius for a given ion. This parameter indicates something about the ability of a cation to coordinate anions about it. A higher ionic potential indicates the ability of one cation type to compete effectively with other cations for available anions to form complex ions such as SiO_4^{-4} in a mixture like coal ash. The values for the ionic potentials of the species of interest are:

Si ⁺⁴	9.52	Fe ⁺²	2.70
Al ⁺³	5.88	Ca ⁺²	2.02
Ti ⁺⁴	5.88	Na ⁺¹	1.06
Fe ⁺³	4.69	K ⁺¹	0.752
Mg ⁺²	2.98		

The highest values belong to the acid group Si, Al, and Ti, while the lowest values belong to the bases.

It is suggested here that the ionic potential may be the physical characteristic which is useful in quantifying acid and base behavior, and would also be useful in future efforts to correlate melting behavior or viscosity with chemical composition.

The ionic potential is a measure of a cation's ability to compete for anions in order to form a complex ion of the form MO_x^{-n} . The ability is also dependent on the available oxide ions. The ability of Si to coordinate four oxide ions would be limited in the pure oxide SiO_2 if it were not for the possibility of sharing oxide ions between different Si. As a result, repeating SiO_2 groups in a V shape can form polymer type groupings. These groupings could be extremely long chains of linked tetrahedra. Other forms are also possible. If additional oxide ions became available, then they would provide the species needed to terminate the chains. As more oxide became available, the groupings would terminate more frequently and have a smaller agglomerate weight. A source for oxide ions would be oxides of cations with low ionic potential such as the alkalis or alkaline earths. These would be expected to dissociate into hard sphere ions, and the oxide ions would be coordinated by cations of the highest ionic potential.

It is suggested that the role of acids in coal ash melts is that of polymer formers with the greatest tendency to form polymers correlating with the greatest ionic potential. The role of bases is that of oxide ion donors. The oxide ions would be attracted to the ions of high potential to break up polymers and reduce viscosity.

In general, the available oxide ions from cations would tend to reduce the size of polymeric groups associated with cations of high ionic potential. Additions of compounds increasing the available oxide ion concentration would decrease the viscosity of a melt rich in Si and Al typical of eastern coal ash material. This effect has already been noted.

The Behavior of Iron

The two valence states of iron give significantly different values with the ferric ion being between the two groups. The special importance of iron can, in part at least, be correlated with the two valences it displays. This may be compared with the amphoteric behavior of certain other species. On the basis of the table of ionic potentials, the ferric ion may be thought of as a weak acid, and the ferrous ion as a base. In practice, the iron in coal ash in boilers will exist as a mixture of the two states. Only a minor part, frequently about 20%, is Fe_2O_3 . The major part (about 80%) is FeO , with possibly some elemental iron. This indicates the appropriateness of classifying iron oxides (if they must be lumped into one type) with the bases, even though they are listed as Fe_2O_3 .

The gaseous environment is important in determining properties of coal ash systems. Studies have shown a marked reduction of viscosity of melts in going from oxidizing to reducing conditions, which would significantly alter the proportion of ferric and ferrous ions. This change in properties would be consistent with a complex ion forming tendency for the ferric ion with its high ionic potential, and an oxide ion donor role for the ferrous ion with its lower ionic potential. Two factors would work to reduce the viscosity in a reducing environment: 1) reduction of concentration of polymer forming ferric ions, and 2) increase in oxide ion concentration available for cations with high ionic potential. The oxide ions would have been associated with the ferrous ions.

Conceptual Structural Considerations

Winegartner and Rhodes³ indicated that the coefficients in front of the bases CaO , MgO , K_2O , and Na_2O should each be one when calculating the softening temperature using the base-to-acid ratio and expressing the ash composition for these materials in mole percentages rather than weight percentages. The implication of that observation in the context of this paper is that the bases are equally effective as oxide ion donors. Each formula contains one oxide unit. They further note that Fe_2O_3 should really be expressed as FeO . This is also consistent with characterizing FeO as a base and indicating the role of oxide ion donor for FeO .

The melting process may be pictured as application of energy to disrupt the crystal lattice of a solid. The lattice of the solid may be modified by the impurities to permit easier melting through introduction of additional large oxide ions in the acid oxide structure. Insertion of base cations would probably occur in the available interstices appropriate for the base coordination number. The resultant lattice strain would yield a lower thermal requirement for melting or a lower melting point. The further implication of Winegartner and Rhodes work is that the number of oxide ions is most significant, and that the nature of the base cations is not significant in affecting the softening temperature.

SUMMARY

The ionic potential (valence divided by ionic radius) may be used as a measure of acids and bases in predicting coal ash melting and viscosity from the chemical composition. The role of an acid is that of a complex ion former with anions provided by bases which in coal ash systems are oxide ion donors. In systems containing acids and limited oxide ion concentrations, polymers tend to form in the melts. Addition of bases reduces polymer size and would decrease viscosity. The gaseous environment may alter the relative concentration of ferric and ferrous ions, interconverting acid and base ions. In general, bases are reported to be equally effective oxide ion donors. The effects of base addition are proportional to the amount of oxide ion provided to the system.

REFERENCES CITED

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